Solar furnace annealing of amorphous Si layers

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We demonstrate that a simple Al solar reflector can be used to induce solid-phase epitaxy of amorphous Si layers obtained either by ion-implantation or ion-deposition techniques. The annealing can be accomplished in air and takes a few seconds for a 1-cm^2 sample area. For ion-implanted samples, the regrown layers are defect free on ⟨100⟩ substrates, and contain microtwins on ⟨111⟩ substrates. For deposited layers on ⟨100⟩ substrates the degree of epitaxy is not as good as that obtained by furnace annealing (550 followed by 950 °C annealing).

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It has been shown that amorphous Si layers obtained by either ion-implantation or ion-deposition techniques on single-crystal substrates can be grown epitaxially by furnace[1,2] or transient (laser or electron-beam) annealing techniques.[3]

In this investigation, we demonstrate that solar energy concentrated by a simple parabolic reflector can be used to convert amorphous Si layers into epitaxial layers in the solid phase. This annealing process requires no vacuum chamber and is capable of annealing large areas in a short time (in our setup, an ~1-cm^2 area can be annealed in a few seconds).

Silicon wafers, ⟨100⟩, and ⟨111⟩ in orientation, were implanted in a random direction with doses of 2×10^{15} $^{28}Si^+/cm^2$ at 100 keV and 1×10^{15} $^{28}Si^+/cm^2$ at 80 keV near liquid-nitrogen temperature. Amorphous layers of about 2000 Å in thickness were created by these implants. Deposition of amorphous Si layers ranging between 1000 and 3000 Å in thickness by e-gun evaporation was also carried out on ⟨100⟩ and ⟨111⟩ Si substrates. The substrates were first degreased in organic solvents, immersed in an RCA solution, etched in a 10% aqueous HF solution, and finally rinsed in high-purity water. After chemical cleaning, the substrates were immediately loaded into a vacuum chamber equipped with ion pumps. Silicon was evaporated at a rate of ~20–50 Å/sec at a pressure $<1\times10^{-6}$ Torr.

The solar furnace consists of a parabolic Al reflector 46 cm in diameter. The sample was positioned at the focal point and thermally isolated. The solar image is about 1.5 mm in diameter and from the data of the parabola a focal intensity of about 1 kW/cm^2 under optimum conditions is estimated.[4] From the solar spectrum and from the optical data of Al it can be concluded that about 70% of the radiation impinging on the sample is at photon energies exceeding the Si band gap. The radiation energy is therefore absorbed in a very thin surface layer. From heat conduction theory, given these conditions, the layer temperature is expected to reach 700 °C within about 0.1 sec. The steady-state temperature, estimated to be on the order of 1000 °C, should be reached within about 1 sec.

Recrystallization of the amorphous Si films was usually accomplished in a few seconds. The recrystallized layers were analyzed by the channeling of MeV-$^4He^+$ particles and transmission electron microscopy (TEM), and compared to furnace annealed samples.

For ⟨100⟩ implanted samples, after about 2 sec of illumination there was a visible color change near the focal point. This color change is associated with the recrystallization of the amorphous layer. This area of changed color spread in size in a circular fashion. To anneal extended areas, the samples were laterally displaced with respect to the focal point at a speed of a few mm/sec. Figure 1 shows the backscattering spectra for a ⟨100⟩ implanted sample illuminated in total for 6 sec. The ⟨100⟩-aligned spectrum shows a 4.3% surface minimum yield, compared to the random yield. (A brief etch of the sample in a dilute HF solution to remove the surface oxide resulted in a 3.5% surface minimum yield.) Transmission-electron-microscopy studies showed little or no defects in the regrown layer.

For deposited layers, on ⟨100⟩ substrates, we found

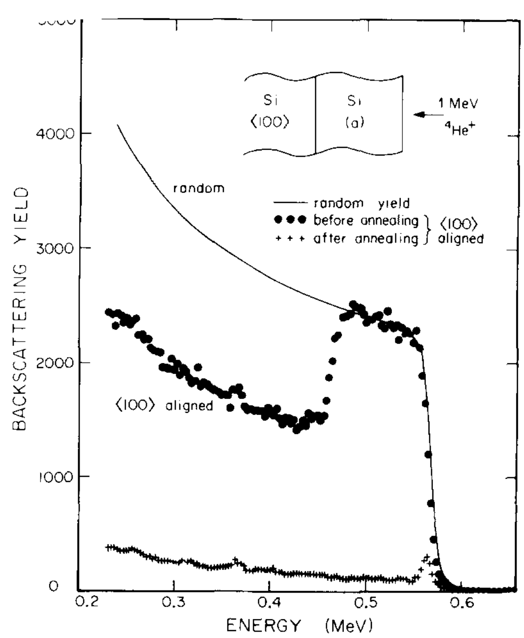

FIG. 1. Backscattering spectra of a ⟨100⟩ sample with ~2000 Å implanted amorphous Si before and after solar annealing for 6 sec.

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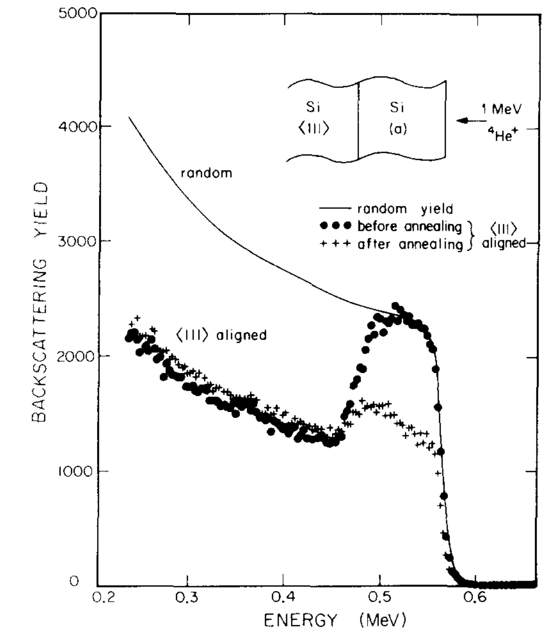

FIG. 2. Backscattering spectra for a 2000 Å ion-implanted amorphous Si layer on ⟨111⟩ substrate before and after solar annealing for 5 sec.

that the solar furnace as well as conventional annealing[2] can be used to induce epitaxy. The crystalline quality of the epitaxial layers annealed with the solar furnace (at ~900–950 °C), however, is not as good as that obtained by conventional furnace annealing at 550 °C. Direct furnace annealing at 950 °C also leads to relatively poor epitaxial layers, but generally better than those annealed by solar energy. This is because samples inserted in a furnace held at 950 °C experience a relatively slow temperature rise. This long rise time allows the epitaxial layer to grow at actually lower temperatures. (The best epitaxial layer can be grown by a two-step annealing process of 550 and 950 °C.[2]

For ⟨111⟩ implanted samples, the regrown layers contain residual damage after illumination. Figure 2 shows the backscattering spectra for a sample before and after 5 sec of illumination. The yield for a ⟨111⟩-aligned incident beam was about 50% of the yield measured at random incidence, which indicates a far inferior single-crystalline quality as compared to the ⟨100⟩ case. This high concentration of residual damage, in the regrown layer revealed to be microtwins by TEM, is very similar to the results obtained from furnace annealing at 550 °C.[1]

It is interesting to note that direct furnace annealing of self-ion-implanted amorphous Si layers on ⟨111⟩ substrates at 950 °C resulted in polycrystal formation,[1] in marked contrast to solar-energy-annealed ⟨111⟩ samples.

We tentatively explain this difference as follows: It is known that a certain incubation period is associated with the onset of spontaneous nucleation and that the nucleation rates are time dependent at a given temperature. The steady-state nucleation is at a maximum rate near 800 °C due to the optimization of undercooling and atomic mobility.[5] The incubation period before the onset of nucleation is inversely related to the steady-state nucleation rate[6] and should exhibit a minimum near 800 °C. If the time to regrow the amorphous layer is short compared to the incubation time at a given growth temperature, no nucleation can occur and the grown layer is epitaxial, as in the case of ⟨100⟩ samples. This concept is sketched in Fig. 3, where the time to regrow a 2000-Å-thick amorphous layer is plotted against temperature schematically for ⟨100⟩ and ⟨111⟩ samples; the incubation time is also included.

For ⟨111⟩ samples, the growth rates are about 20 times slower than those observed on ⟨100⟩ samples in the temperature range of 500–600 °C. Samples inserted directly into a furnace held at 900–950 °C usually need a time of the order of a few minutes before the preset temperature is reached. During this slow temperature rise, the growth temperature falls within the range in Fig. 3 where nucleation is faster than growth. Therefore, nucleation of crystallites in the amorphous layer occurs before the consumption of the entire layer by epitaxial growth. Under such conditions, polycrystals are formed. On the other hand, if the high annealing temperature (i.e., 950 °C) can be achieved instantaneously or in a very short time, as in the case of solar-energy annealing where the rise time is of the order of 0.1 sec, the entire amorphous layer is regrown before spontaneous nucelation can take place. The residual disorder (only twins and not polycrstallites) in the regrown layer is an intrinsic behavior of ⟨111⟩ solid-phase regrowth and not due to nucleation.[1]

Table I summarizes the results of epitaxial growth induced by different methods. The typical annealing time ranges between 10^{-8} sec and hours. For the fastest annealing time (i.e. ~ 10^{-8} sec), the epitaxial growth is believed to be in the liquid phase. For long annealing times, the growth is believed in the solid phase.

In conclusion, we have demonstrated that a simple solar furnace can be used to induce solid-phase epitaxial growth of a few-thousand-Å-thick amorphous Si layer in a few seconds over cm^2 areas. For implanted layers, solar furnace annealing produces equal or better epitaxial layers than those obtained from conventional furnace annealing. For de-

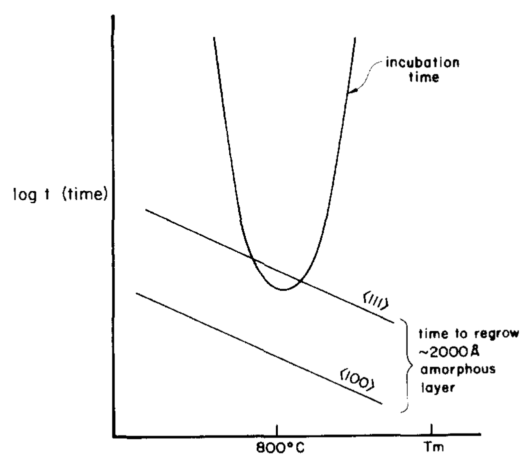

FIG. 3. Schematics of log$t$ (either time to regrow an amorphous layer of given thickness, or incubation time before nucleation of crystallites) versus temperature.

TABLE I. Summary of epitaxial growth results on silicon.

Substrate orientation (typical annealing time)	Si amorphous layer	Laser Anneal: Q-switched and PEBA [a] (10^{-8} sec)	Laser Anneal: Scanning laser (10^{-3} sec)	Solar illumination (sec)	Furnace Anneal: 950 °C (min)	Furnace Anneal: 550 °C (h)
⟨100⟩	Self-ion implanted	Good epitaxy $\chi_{min} \sim 4\%$ (Ref. 8)	Good epitaxy $\chi_{min} \sim 4\%$ (Ref. 9)	Good epitaxy $\chi_{min} \sim 4\%$	Good epitaxy $\chi_{min} \sim 4\%$ (Ref. 1)	Good epitaxy $\chi_{min} \sim 4\%$ (Ref. 1)
	Evaporated	Good epitaxy $\chi_{min} \sim 5\text{–}6\%$ (Ref. 7)	No successful results reported	Poor epitaxy $\chi_{min} \sim 60\%$ Planar defects at the original film substrate interface	Fair epitaxy $\chi_{min} \sim 7\%$ Planar defects at the original film substrate interface (Ref. 2)	Fair epitaxy $\chi_{min} \sim 4\text{–}5\%$ Planar defects at the original film substrate interface (Ref. 2)
⟨111⟩	Self-ion implanted	Good epitaxy $\chi_{min} \sim 4\%$ (Ref. 8)	Poor epitaxy similar to furnace anneal at 550 °C (amorphous layer created by As-ion implantation (Ref. 9))	Poor epitaxy $\chi_{min} \sim 50\%$ (Ref. 8)	Polycrystal (Ref. 1)	Poor epitaxy, variation of planar defects in regrown layer (Ref. 1)
	Evaporated	Poor epitaxy $\chi_{min} \sim 50\%$ (Ref. 10)	No successful results reported	Very poor epitaxy $\chi_{min} \sim 90\%$	Not successful at present	Not successful at present

[a]Pulsed electron-beam annealing.

posited layers, thermal annealing at lower temperatures produces better epitaxial layers.

The relevant finding in this investigation is the fact that the fast heating of samples can lead to better epitaxy. We believe that rapid annealing of implanted layers either with the sun or any thermal light source or hot liquid immersion can have potential applications. Since growth can be induced in the solid phase, no redistribution of dopants is expected. On-site annealing of ion-implanted solar cells could be an interesting application.

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